EVALUATION OF ALUMINUM CORROSION AND COMPOSITE HEAT DAMAGE USING MAGNETIC RESONANCE NDE

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INTRODUCTION

Magnetic resonance nondestructive evaluation (NDE) methods are being used successfully in the medical, biological and petroleum industries due to their sensitivity to human tissue and other fluid materials. Application to NDE of solid materials, such as those utilized in the aerospace industry, has been limited due to the lower resolution and increased bandwidth of the measurements. With the recent development of measurement techniques and instrumentation appropriate for the NDE of solids, the sensitivity of NMR applied to solid materials has improved; as a result, increasing attention is now being given to the technique's ability to evaluate aerospace materials and structures. During this program [1], magnetic resonance techniques were found to be useful for evaluation of corrosion in aluminum and heat damage in composite materials. In a previous study [2], corrosion and heat damage were shown to be detectable using nuclear magnetic resonance (NMR). In this program, these phenomena were evaluated in greater detail using additional NMR parameters and the electron spin resonance (ESR) technique.

BACKGROUND

NMR is a physical technique that forms the basis for magnetic resonance imaging (MRI), a fully developed nondestructive inspection method for living systems. Based on the interaction of nuclear magnetic moments with an external field, NMR is a spectroscopic tool that is sensitive to (and provides information about) atomic motion, chemical structure, and the presence of paramagnetic impurities, such as unpaired electrons. Although it is limited by skin depth effects in conductors (typical frequencies are 1-100 MHz), NMR can be used on bulk dielectrics and to provide information about surface damage of conductors. An NMR apparatus consists of a magnet, a tuned circuit (antenna), and a fast recovery RF spectrometer (pulsed transmitter and receiver), not unlike ultrasonic inspection equipment.

NMR is usually performed with large, superconducting magnets and high-power RF amplifiers. However, NMR experiments can also be performed with smaller, hand-held permanent or electromagnets for field inspection purposes. In fact, smaller magnetic fields

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imply lower NMR frequencies which, in turn, translate to larger skin depths. The entire NMR RF equipment set can easily fit into a five inch high standard rack box. For a field inspection, it is not be necessary to wrap the sample in an NMR coil; surface coils perform well [3].

There are several parameters which characterize the NMR signals that were used here to differentiate between pristine materials and their damaged or corroded counterparts. The Knight shift has been demonstrated to be capable of differentiating between corroded aluminum and aluminum metal; it is expected that the spin-spin relaxation time (T_2) can do the same. In addition, an unexpected hydrogen NMR signal is a clear identifier of the presence of aluminum corrosion. Heat damaged carbon/epoxy differs from undamaged material by the magnitude of its spin-lattice relaxation time (T_1) and the presence of an ESR signal.

EXPERIMENTAL METHODS

Magnetic Resonance Evaluation

T_1 is the time constant that characterizes the nuclear magnetization's recovery toward it's equilibrium value parallel to the external magnetic field. In this study, T_1 was defined by standard saturation-recovery sequences. T_2 characterizes the decay of the NMR signal itself and was defined by the time to decay by a factor of 2.72 [4].

The Knight shift is a shift of the NMR frequency of a metal due to interactions with conduction electron spins in a metal. Knight shift measurements were made from frequency domain spectra, acquired by Fourier transforming an aluminum quadrupolar echo.

ESR is a spectroscopic technique which directly examines the interaction of unpaired electron magnetic moments with an external magnetic field. As a result, it is sensitive to the presence of free radicals (unpaired electrons) resulting from a chemical change in a system. ESR amplitudes reported are from peak-to-trough of the ESR derivative signal.

Material Specimens

To evaluate the aluminum corrosion phenomenon, four aluminum specimens were evaluated: (1) corrosion particles scraped from a corroded aluminum fuselage section, (2) aluminum hydroxide specimen provided as $Al(OH_3)\bullet nH_2O$ in an unspecified state of hydration, (3) epoxy adhesive specimen taken from between bonded sheets of corroded aluminum and (4) low purity laboratory grade aluminum oxide packed around a strip of aluminum foil.

To assess the potential of heat damage detection, undamaged, partially damaged and severely damaged specimens of the following material types were evaluated: (1) AS4/3501-6 carbon/epoxy and (2) T300/V378A carbon/bismaleimide. Damage was incorporated by prolonged surface heating using a quartz lamp.

RESULTS AND DISCUSSION

Characterization of Aluminum Corrosion Products

Differences in the chemical composition of aluminum and aluminum corrosion products lead to: (1) different aluminum NMR frequencies for the metal and corrosion signals, (2) different aluminum NMR time constants (T_1 and T_2) and signal shapes and (3) the presence of a hydrogen signal from water of hydration and/or hydroxide groups. All three of these were used to detect the presence of aluminum corrosion using NMR.

In a 2 Tesla field (22.1 MHz for ^{27}Al), the frequency difference (Knight shift) between the peak of a metallic aluminum line and the peak of an aluminum oxide line was measured to be about 35.6 kHz (0.16%). These lines are shown in Figure 1. Clearly, in this field strength, where the two lines are well resolved, the detection of aluminum corrosion is a trivial matter of separating the two aluminum NMR lines. At lower fields, the separation between the two lines will decrease linearly with the field and the full width-half maximum (FWHM) of the aluminum oxide line will increase (due to quadrupole effects), making differentiation more difficult. Nevertheless, it is expected that with an external magnetic field greater than 1 Tesla, the Knight shift provides an adequate way of discriminating aluminum corrosion.

A comparison between aluminum NMR signals from corroded aluminum and aluminum hydroxide hydrate ($Al(OH_3)\bullet nH_2O$) was performed. T_2 was measured from the spin-echo decay envelope; the values for both specimens were similar: 252 ms for the aluminum corrosion and 282 ms for the aluminum hydroxide hydrate. However, these measurements, performed at 22.1 MHz (2.0 Tesla) in an aluminum-free probe, were made with only a few data points and need to be evaluated more thoroughly. Metallic aluminum is expected to have a very short T_2 because of the higher aluminum density in the metal in comparison with the corrosion product. The local magnetic fields due to surrounding nuclei are larger in the material with the higher density. This results in an increase in linewidth, which translates to decreased T_2 because of the reciprocal relationship between frequency and time.

Because of its longer T_2, aluminum corrosion is still expected to form detectable quadrupolar echoes at times near one-half millisecond after the initial NMR pulse; by comparison, aluminum metal should not form echoes for nearly as long a time. The ability to form an Al NMR echo one-quarter to one-half millisecond after the initial pulse can be used to differentiate the aluminum corrosion signal from that of aluminum metal.

Aluminum corrosion is not just aluminum oxide; other aluminum products are present as well, such as aluminum hydroxide [5]. In addition, the corrosion products may be hydrated. In fact, a hydrogen NMR signal was seen from the corroded aluminum, indicating the presence of compounds besides pure aluminum oxide. This was compared

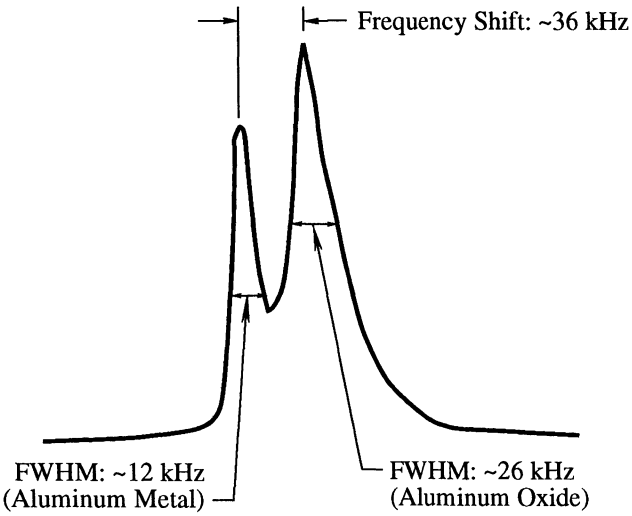

Figure 1. Aluminum-27 NMR spectra of specimen containing aluminum metal and aluminum oxide (field strength = 2.0 Tesla).

with the signal obtained from the aluminum hydroxide hydrate; the hydrogen NMR signals from both of these specimens were similar. Both had short and long T_2 components.

To determine whether the hydrogen NMR signal from the corrosion was coming from components of a nearby epoxy adhesive sheet, a sample of epoxy adhesive was taken from the fuselage panel and T_2 was measured. The signals from this material had a single FID with a short T_2 decay time, and were easily distinguished from the two-component hydrogen signal from the aluminum corrosion. T_1 was also measured for each specimen, with resulting data presented in Table 1. T_1 for the aluminum corrosion specimen was a relatively short 2.1 ms. This short T_1 value will allow for rapid signal averaging.

From the similarities in both the hydrogen and aluminum NMR data for aluminum corrosion and aluminum hydroxide hydrate, it can be concluded that the aluminum corrosion specimen is chemically similar to the $Al(OH)_3 \bullet nH_2O$. This indicates that it will be possible to evaluate an aluminum structure for corrosion by looking for the hydrogen NMR signal from the hydroxide groups and water molecules present in the corrosion product.

Clearly, the presence of a hydrogen NMR signal holds promise as a sensitive technique for detecting aluminum corrosion products on an aluminum surface where hydrogen nuclei are not expected to be present. Because hydrogen has an NMR frequency four times that of aluminum, the sensitivity of a hydrogen NMR signal is greater than an aluminum signal and would yield a greater probability of detection.

Characterization of Heat Damage in Composite Materials

Overheating a composite material can cause damage by breaking chemical bonds and can subsequently cause reductions in mechanical strength. The resultant unpaired electrons (free radicals) create fluctuating magnetic fields which can relax the magnetic spins of nearby nuclei. The overall effect is a decreased spin-lattice relaxation time, T_1, in the damaged polymers. Furthermore, whereas paired electron spins have no net magnetic moment and do not produce an electron spin resonance signal, unpaired electrons produce a strong ESR signature.

For this evaluation, characterizations of carbon/epoxy and carbon/bismaleimide materials were performed. The goal was to establish the effects of heat damage upon the materials' NMR signatures; to this end, T_1 was measured in specimens of each material. The results of these measurements are contained in Table 2.

Table 1. Hydrogen NMR spin-lattice and spin-spin relaxation times for aluminum compounds.

Material	T_1 (ms)	Short T_2 (μs)	Long T_2 (μs)
Aluminum Corrosion Product	2.4	10.0	136.8
Aluminum Hydroxide-Hydrate	220.0	9.8	130.6
Epoxy Adhesive Sheet	220.0	21.9	--

-- No Long T_2 Component

Table 2. Basic NMR constants for undamaged and damaged carbon composite materials at 85 MHz.

Material	T_1 (s)	T_2 (μs)
Carbon/Epoxy:		
No Damage	1.00	11.0
Slight Damage	0.55	10.7
Severe Damage	0.27	13.2
Carbon/Bismaleimide:		
No Damage	0.37	13.6
Slight Damage	0.39	13.3
Severe Damage	0.29	14.9

The hydrogen T_1 measured fro the damaged material was a factor of four smaller than T_1 measured in the undamaged state. Furthermore, the T_1 recovery curve of the damaged material had a more pronounced multi-exponential character than did that of the undamaged material. The T_1 magnitude of the partially damaged specimen was intermediate between the damaged and undamaged region; it was a factor of two shorter than the undamaged material and a factor of two greater than the damaged material, as shown in Figure 2. The recovery curve was not a single exponential function, which suggests that the specimen may have contained both damaged and undamaged regions or is at least spatially inhomogeneous.

The decrease in T_1 of the damaged material was most likely due to an increase in free radical concentration that occurs when the epoxy is overheated. The resultant broken bonds and unpaired electrons (which have magnetic moments three orders of magnitude larger than the moments of the nuclei) act as relaxation centers for the hydrogen and thereby, decrease T_1. This change in T_1 is substantial and suggests that it should not be difficult to characterize heat damage in carbon/epoxy composites using NMR.

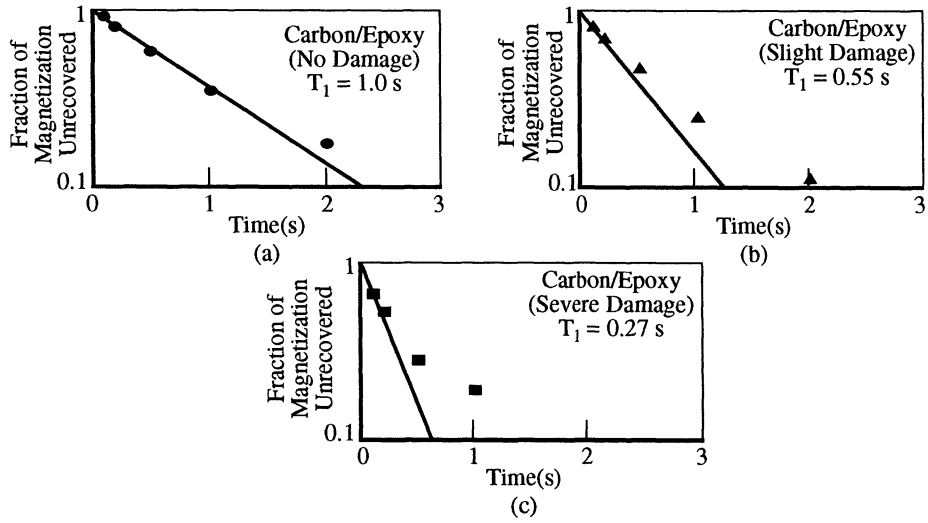

Figure 2. Magnetization recovery curves for carbon/epoxy with (a) no damage, (b) slight damage and (c) severe damage.

For carbon/bismaleimide, the hydrogen T_1 change in the heat damaged material was much smaller (about 25%). The primary difference between damaged and undamaged material was that the undamaged material had a T_1 recovery curve which was nearly single exponential while the damaged material's T_1 recovery curve was markedly multi-exponential. In fact, when T_1 was defined as the time to recover to 1/e of equilibrium, which shows the average T_1 for the whole specimen, the T_1 values of the damaged and undamaged materials were very similar. The slight variations in T_1 values reported here were determined from the initial slope of the T_1 recovery curve. This method is weighted more heavily by the T_1 of the fastest relaxing nuclei in the specimen. This is the T_1 measurement method which would be most sensitive to decreases in T_1 in select portions of the specimen, such as regions near free radicals.

ESR measurements were performed in order to determine whether there had been an increase in free radicals when the materials were damaged by heat. The resultant ESR spectra are shown in Figure 3, with the data summarized in Table 3. ESR signals indicate the presence of unpaired electrons and are, therefore, a direct measure of free radicals. It is clear that there are few, if any, free radicals in the undamaged carbon/epoxy specimen. On the other hand, the damaged carbon/epoxy material yielded a strong ESR signal. The results show that the overheating has indeed caused the formation of free radicals in the carbon/epoxy material.

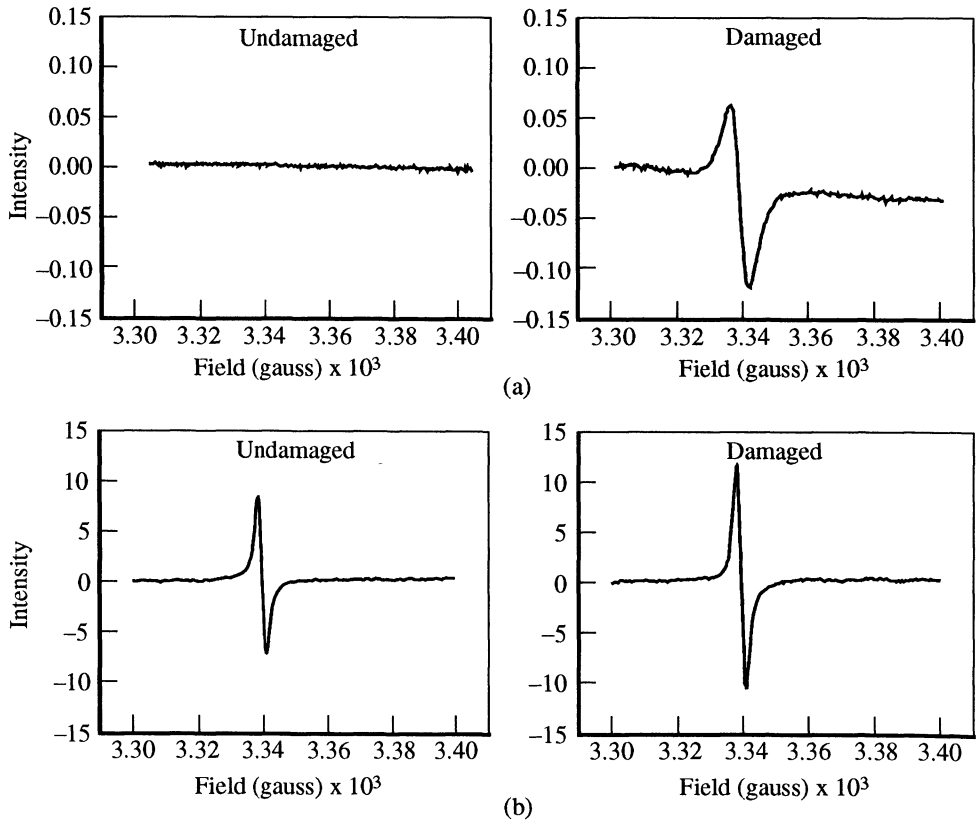

Figure 3. ESR spectra for undamaged and damaged composite materials at 9.38 GHz: (a) carbon/epoxy, (b) carbon/bismaleimide.

Table 3. ESR signal amplitudes for undamaged and damaged composite materials at 9.38 GHz.

Material	Normalized Signal
Carbon/Epoxy:	
No Damage	0.0
Severe Damage	6.7
Carbon/Bismaleimide:	
No Damage	2100.0
Severe Damage	2400.0

The results were somewhat different for the carbon/bismaleimide material. Both damaged and undamaged carbon/bismaleimide have strong ESR signals. These signals are several hundred times stronger than those seen for damaged carbon/epoxy. The signal of the damaged material is slightly larger than that of the undamaged material; however, the difference is within experimental error.

The use of ESR to characterize heat damage in carbon/epoxy materials is promising. In fact, ESR could prove to be a more sensitive evaluation tool than using NMR spin-lattice relaxation measurements. ESR would potentially yield a go-no go test using the signal amplitude as a measure of damage.

CONCLUSIONS

Aluminum corrosion is chemically similar to aluminum hydroxide hydrate. Because it contains hydrogen, it is feasible to detect corroded aluminum by observing for a hydrogen NMR signal that would not be present with non-corroded aluminum. The unusually long T_2 and short T_1 of the hydrogen signal from aluminum corrosion will allow this signal to be distinguished from signals of nearby rigid polymers and from pooled fluids. Detecting the hydrogen NMR signal will result in much greater signal strength than detection of the ^{27}Al nucleus using NMR. This equates to more rapid detection and evaluation.

The Knight shift between aluminum and corrosion and aluminum metal allows aluminum NMR to differentiate between corroded and non-corroded materials, but only in fields of 1 Tesla or greater. As the field strength is reduced, the linewidth of the corrosion products increases due to second order quadrupolar effects while the Knight shift decreases. Only in fields of 1 Tesla or greater will the lines be spectrally resolvable. In addition, T_2 differences may allow for differentiation between metallic aluminum and aluminum corrosion products. Thus, it is possible to distinguish aluminum metal from aluminum corrosion by aluminum NMR frequency, aluminum NMR relaxation times and the presence/absence of a hydrogen NMR signal.

Heat damage generates a high concentration of free radicals in carbon/epoxy materials. The decrease of hydrogen T_1 and/or the presence of an ESR signal can be used to differentiate between thermally damaged carbon/epoxy and its undamaged counterparts. In fact, the hydrogen T_1 of heat damaged carbon/epoxy decreased by a factor of four, allowing unambiguous detection of heat damage. Also, for carbon/epoxy systems, the ESR signal amplitude was found to increase by two orders of magnitude in the heat damaged state. This suggests that an inspection technique using ESR would be extremely sensitive to changes caused by thermal exposure. This increased sensitivity is due to the large magnetic moments associated with electron spins.

For carbon/bismaleimide systems, magnetic resonance detection of heat damage was more difficult to interpret. Bismaleimide resin systems characteristically have free radicals present in their cured state. Small changes in NMR parameters and an increase in ESR signal amplitude are noted; however, it is unclear whether these changes can be used to reliably discriminate between undamaged and damaged carbon/bismaleimide systems.

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